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1. Untranslatable words are replaced with asterisks (***).
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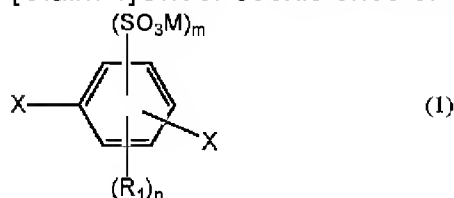
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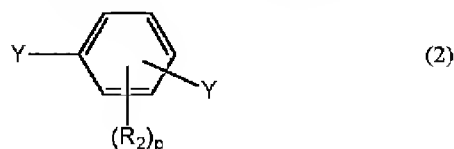
CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] Under coexistence of zerovalent transition metal complex, it is a lower type (1).



(X express chlorine, bromine, and iodine atom among a formula, and M expresses an alkali metal or the 4th class ammonium.) m expresses 1 or 2 and n expresses 4-m. R_1 may differ mutually, when a substituent which does not participate in a hydrogen atom or a polymerization reaction is expressed and there is two or more R_1 . The dihalogeno benzenesulfonic acid and a lower type (2) which are made polymerize the dihalogeno benzenesulfonic acid shown or shown by a formula (1)



(Y expresses chlorine, bromine, and iodine atom among a formula, and p expresses 1-4.) R_2 may differ mutually, when a substituent which does not participate in a hydrogen atom or a polymerization reaction is expressed and there is two or more R_2 . A form of a free acid making dihalogeno benzenes shown copolymerize is a lower type (3).

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ACC-NO:

DERWENT- 200817

WEEK:

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TITLE: Manufacture of polyphenylene sulfonic acid used for electrolyte film, involves (co)polymerizing dihalogeno benzenesulfonic acid and dihalogeno benzene in presence of zero valent transition metal complex

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PRIORITY-DATA: 2002JP-044343 (February 21, 2002)

PATENT-FAMILY:

| PUB-NO | PUB-DATE | LANGUAGE |
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| JP 2003238665 A | August 27, 2003 | JA |
| JP 4051955 B2 | February 27, 2008 | JA |

**INT-CL-
CURRENT:**

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ABSTRACTED-PUB-NO: JP 2003238665 A

BASIC-ABSTRACT:

NOVELTY - A dihalogeno benzene sulfonic acid and dihalogeno benzene are (co)polymerized in the presence of a zero valent transition metal complex, to obtain a polyphenylene sulfonic acid in the form of free acid.

DESCRIPTION - A dihalogeno benzene sulfonic acid of formula (1) and dihalogeno benzene of formula (2) are (co)polymerized in the presence

of zero valent transition metal complex, to obtain a polyphenylene sulfonic acid of formula (3) in the form of free acid.

X,Y = chlorine, bromine or iodine atom;

M = alkali metal or quaternary ammonium;

m = 1 or 2;

n = 4-m;

R1,R2 = substituent which does not contain hydrogen atom or used in polymerization reaction; and

p = 1-4.

R1,R2,m,n,p = same as defined above; and

q,r = number of repeating units, ratio of r with respect to q is 0-100, and sum of q and r is 10-100000.

An INDEPENDENT CLAIM is included for the polyphenylene sulfonic acid.

USE - Used for electrolyte film for fuel cell (both claimed), and as polyelectrolyte for solid polymeric type fuel cells.

ADVANTAGE - The manufacturing method enables to produce polyphenylene sulfonic acid readily. The electrolyte film containing the polyphenylene sulfonic acid exhibits properties similar to a diaphragm, in polymeric type fuel cell.

EQUIVALENT-ABSTRACTS:

INORGANIC CHEMISTRY

Preferred Compounds: A zero valent transition metal complex is zero valent nickel complex and/or zero valent palladium complex.

Preferred Method: The manufacturing method of polyphenylene sulfonic acid further uses 2-2'-bipyridyl as a ligand.

SPECIFIC COMPOUNDS

The zero valent nickel complex is nickel(0) bis (cyclo octadiene).

Dimethyl formamide (120 ml), 2,5-dichloro benzene sulfonic acid (1.33 g), 2,2'-bipyridyl (1.84 g) were added and stirred in argon atmosphere. Nickel(0)bis(cyclo octadiene (3.2 g) was added and stirred at 60 degreesC for 3 hours to obtain a reaction solution. The

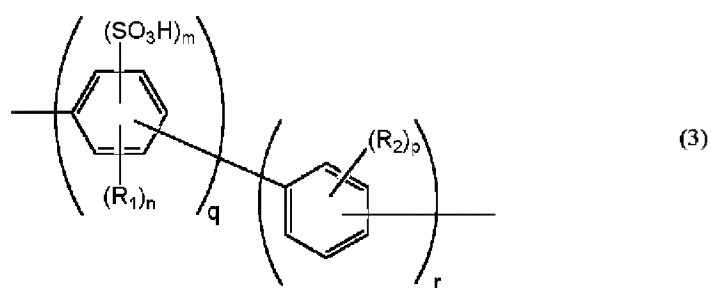
obtained reaction solution was cooled and poured into methanol, to precipitate a crude polymer. The crude polymer was dissolved in water and the insoluble content was separated by filtration. The filtrate was concentrated and re-precipitated using methanol. The filtrate was dried under reduced pressure to obtain a polyphenylene sulfonic acid (0.56 g). The polyphenylene sulfonic acid had weight average molecular weight of 2700 and molecular distribution of 2300.

Derwent Accession Number - NRAN (1):

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Patent Family Serial Number - PFPN (1):

2003238665



(R_1 , R_2 , m , n , and p express an above meaning among a formula.) q and r express the number of repeating units, and a repeating unit whose ranges of a ratio of r to the range of 10-100000 and q are the sum of q and r 0-100 and which has q pieces, and r repeating units may be the same respectively, or may differ from each other. A manufacturing method of poly-phenylene-sulfone acids shown.

[Claim 2]The manufacturing method according to claim 1, wherein zerovalent transition metal complex is at least one sort chosen from a zerovalent nickel complex and a zero valent palladium complex.

[Claim 3]The manufacturing method according to claim 2, wherein a zerovalent nickel complex is a nickel (0) screw (cyclo-octadiene).

[Claim 4]The manufacturing method according to any one of claims 1 to 3 which makes 2,2'-bipyridyl live together as a ligand furthermore.

[Claim 5]Poly-phenylene-sulfone acids shown by said formula (3) obtained by a method of one of Claims 1-4.

[Claim 6]An electrolyte membrane which consists of the poly-phenylene-sulfone acids according to claim 5.

[Claim 7]A fuel cell which uses an electrolyte membrane of Claim 6.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of poly-phenylene-sulfone acids, and relates to the manufacturing method of the poly-phenylene-sulfone acids by making dihalogeno benzenesulfonic acid polymerize or copolymerize in detail.

[0002]

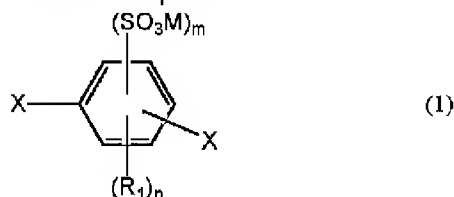
[Description of the Prior Art]Poly-phenylene-sulfone acids being useful as polyelectrolyte for polymer electrolyte fuel cells, etc., manufacturing polymer as the manufacturing method using the monomer which does not have a sulfonic group probably, and manufacturing by subsequently sulfonating this is also known. For example, the method of sulfonation poly (4'-phenoxybenzoyl) (-1,4-phenylene) manufacturing poly (4'-phenoxybenzoyl) (-1,4-phenylene),

and manufacturing by subsequently sulfonating this is known (US,5403675,B). The sulfonation thing of the random copolymer of Para Feni Wren and meta-phenylene manufacturing this copolymer, and manufacturing by subsequently sulfonating this is known (Polymer Preprints, Japan, Vol.50, No.4, (2001)). However, about how to manufacture poly-phenylene-sulfone acids at once, it is not known at all using the monomer which has a sulfonic group.

[0003]

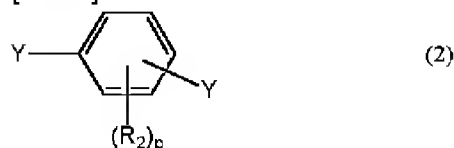
[Means for solving problem]The result of having repeated examination wholeheartedly this invention persons manufacturing poly-phenylene-sulfone acids at once using the monomer which has a sulfonic group, It might polymerize under coexistence of zerovalent transition metal complex, a specific monomer called dihalogeno benzenesulfonic acid added further various examination, while finding out giving poly-phenylene-sulfone acids at once, and it completed this invention.

[0004]That is, it is a lower type (1) under coexistence of this invention and zerovalent transition metal complex.



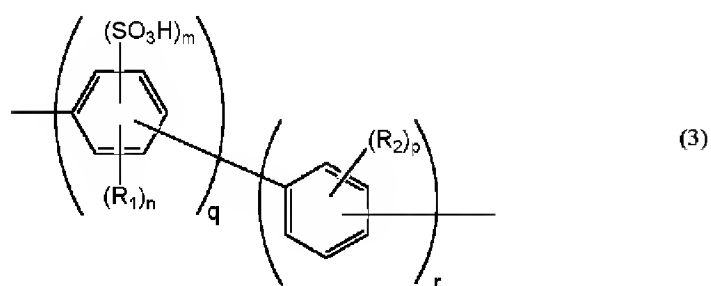
[0005](X express chlorine, bromine, and iodine atom among a formula, and M expresses an alkali metal or the 4th class ammonium.) m expresses 1 or 2 and n expresses 4-m. R_1 may differ mutually, when the substituent which does not participate in a hydrogen atom or a polymerization reaction is expressed and there is two or more R_1 . The dihalogeno benzenesulfonic acid and the lower type (2) which are made polymerize the dihalogeno benzenesulfonic acid shown or shown by a formula (1)

[0006]



(Y expresses chlorine, bromine, and iodine atom among a formula, and p expresses 1-4.) R_2 may differ mutually, when a substituent which does not participate in a hydrogen atom or a polymerization reaction is expressed and there is two or more R_2 . A form of a free acid making dihalogeno benzenes shown copolymerize is a lower type (3).

[0007]



(R_1 , R_2 , m , n , and p express an above meaning among a formula.) q and r express the number of repeating units, and, [the sum of q and r] Ranges of a ratio of r to the range of 10-100000 and q are 0-100, and q repeating units and r repeating units may be the same respectively, or may differ from each other. A manufacturing method which was industrially excellent in polyphenylene-sulfone acids shown is provided.

[0008]

[Mode for carrying out the invention] Hereafter, this invention is explained in detail. The dihalogeno benzenesulfonic acid shown by said formula (1) under coexistence of this invention and zerovalent transition metal complex is made to polymerize. Although X in dihalogeno benzenesulfonic acid (1) expresses chlorine, bromine, and iodine atom, it is preferred that it is a bromine atom. M expresses an alkali metal or the 4th class ammonium. Here, as an alkali metal, lithium, sodium, potassium, etc. are mentioned, for example. As the 4th class ammonium, what about 12 alkyl groups [four] combined with a nitrogen atom from the carbon number 1 is usually used. these alkyl groups may differ -- straight chain shape and branched state -- annular -- they may be any. As a desirable example of the 4th class ammonium, tetramethylammonium, tetraethylammonium, tetrapropylammonium, and tetrabutylammonium are mentioned, for example. When solubility to an organic solvent is taken into consideration, the 4th class ammonium is more preferred and tetrabutylammonium is more preferred in the latter than in an alkali metal.

[0009] As for m , one is preferred, although m expresses 1 or 2 and n expresses 4- m . R_1 may differ mutually, when the substituent which does not participate in a hydrogen atom or a polymerization reaction is expressed and there is two or more R_1 . As an example of R_1 , for example Methyl, ethyl, n -propyl, Isopropyl, isoamyl, 2-methylhexyl, 2,6-dimethyloctyl, The straight chain of the carbon numbers 1-12, such as n -decyl and n -dodecyl, the alkyl group of annular or branched state, Methoxy and ethoxy ** n -propyloxy, isopropyloxy, isoamyl oxy, 2-methylhexyl oxy, 2,6-dimethyl octyloxy, n -decyloxy, The straight chain of the carbon numbers 1-12, such as n -dodecyloxy, the alkoxy group of annular or branched state, The group of carboxylic acid derivatives, such as a hydroxyl group, carbomethoxy, ethoxycarbonyl, isopropoxycarbonyl, aminocarbonyl, and N,N -dimethylamino carbonyl, a fluorine atom, etc. are mentioned. The alkyl group and alkoxy group which an alkyl group, an alkoxy group, a fluorine

atom, etc. are especially preferred, and have many carbon numbers have an effect in the soluble improvement in poly-phenylene-sulfone acids. It is mentioned.

[0010][as an example of representation of dihalogeno benzenesulfonic acid (1)] For example, 2,4-dichloro benzenesulfonic acid, 2,5-dichloro benzenesulfonic acid, 2,4-dibromo benzenesulfonic acid, 2,5-dibromo benzenesulfonic acid, 2,4-diiodo benzenesulfonic acid, 2,5-diiodo benzenesulfonic acid, A 2,4-dichlorobenzene 1,5-disulfon acid, a 2,5-dichlorobenzene 1,4-disulfon acid, A 2,4-dibromo benzene-1,5-disulfon acid, a 2,5-dibromo benzene-1,4-disulfon acid, 2,4-dichloro-5-methylbenzene sulfonic acid, 2,5-dichloro-4-methylbenzene sulfonic acid, 2,4-dibromo-5-methylbenzene sulfonic acid, 2,5-dibromo-4-methylbenzene sulfonic acid, 2,4-dichloro-5-methoxy benzenesulfonic acid, 2,5-dichloro-4-methoxy benzenesulfonic acid, Alkali metal salt and quarternary ammonium salt, such as 2,4-dibromo-5-methoxy benzenesulfonic acid and 2,5-dibromo-4-methoxy benzenesulfonic acid, are mentioned.

[0011]In this invention, when making it copolymerize with dihalogeno benzenesulfonic acid (1), dihalogeno benzenes (2) is used. Although Y in dihalogeno benzenes (2) expresses chlorine, bromine, and iodine atom, it is preferred that it is a bromine atom. p expresses 1-4. R_2 may differ mutually, when the substituent which does not participate in a hydrogen atom or a polymerization reaction is expressed and there is two or more R_2 . As an example of R_2 , for example Methyl, ethyl, n-propyl, Isopropyl, isoamyl, 2-methylhexyl, 2,6-dimethyloctyl, The straight chain of the carbon numbers 1-12, such as n-decyl and n-dodecyl, the alkyl group of annular or branched state, Methoxy and ethoxy **n-propyloxy, isopropyloxy, isoamyl oxy, 2-methylhexyl oxy, 2,6-dimethyl octyloxy, n-decyloxy, The straight chain of the carbon numbers 1-12, such as n-dodecyloxy, the alkoxy group of annular or branched state, The group of carboxylic acid derivatives, such as a hydroxyl group, carbomethoxy, ethoxycarbonyl, isopropoxycarbonyl, aminocarbonyl, and N,N-dimethylamino carbonyl, a fluorine atom, etc. are mentioned. The alkyl group and alkoxy group which an alkyl group, an alkoxy group, a fluorine atom, etc. are especially preferred, and have many carbon numbers have an effect in the soluble improvement in poly-phenylene-sulfone acids.

[0012][as an example of representation of dihalogeno benzenes (2)] For example, 2,4-dichlorotoluene, 2,5-dichlorotoluene, 2,4-dibromo toluene, 2,5-dibromo toluene, 2,4-dichloro anisole, 2,5-dichloro anisole, 2,4-dibromo anisole, 2,5-dibromo anisole, 2,4-dichloro-1-isoamyl oxybenzene, 2,5-dichloro-1-isoamyl oxybenzene, 2,4-dibromo-1-isoamyl oxybenzene, 2,5-dibromo-1-isoamyl oxybenzene, 2,4-dichloro-1-(2,6-dimethyl octyloxy) benzene, 2,5-dichloro-1-(2,6-dimethyl octyloxy) benzene, 2,4-dibromo-1-(2,6-dimethyl octyloxy) benzene, 2,5-dibromo-1-(2,6-dimethyl octyloxy) benzene, 2,5-dichloro-4-isoamyl oxyanisole, 2,5-dibromo-4-isoamyl oxyanisole, 2-fluoro-1,4-dichlorobenzene, 2-fluoro-1,4-dibromo benzene, 2,5-difluoro-1,4-dichlorobenzene, 2,5-difluoro-1,4-dibromo benzene, 2,3,5,6-tetrafluoro 1,4-

dichlorobenzene, 2,3,5,6-tetrafluoro 1,4-dibromo benzene, etc. are mentioned.

[0013]Although this invention makes a polymerization or dihalogeno benzenesulfonic acid (1), and dihalogeno benzenes (2) copolymerize, [this invention] [under coexistence of zerovalent transition metal complex] [the above dihalogeno benzenesulfonic acid (1)] As this zerovalent transition metal complex, a zerovalent nickel complex, a zero valent palladium complex, etc. are mentioned, for example. A zerovalent nickel complex is used preferably especially. As a zero valent palladium complex, palladium (0) tetrakis (triphenyl phosphine) etc. are raised, for example. As a zerovalent nickel complex, nickel (0) screw (cyclo-octadiene) and nickel (0) (ethylene) bis(triphenyl phosphine)nickel (0) tetrakis (triphenyl phosphine) etc. are mentioned, for example. It is preferred for a nickel (0) screw (cyclo-octadiene) to be used preferably, and to make neutral ligand live together further in this case especially, and, [as this ligand] For example, 2,2'-bipyridyl, 1,10-phenanthroline, methylenescrew oxazoline, Tertiary phosphine ligands, such as nitrogen-containing ligands, such as N,N'-tetramethylethylenediamine, triphenyl phosphine, tritolyl phosphine, tributyl phosphine, and triphenoxy phosphine, etc. are mentioned. A nitrogen-containing ligand is preferred and especially 2,2'-bipyridyl is especially preferred. as opposed to the monomer which uses zerovalent transition metal complex -- usually -- about 0.1-5 mol twice -- about 1-3 mol is used preferably. moreover -- receiving a transition metal, when using a ligand -- usually -- about 0.2-2 mol twice -- it is used about 1 to 1.5 times preferably.

[0014]When manufacturing dihalogeno benzenesulfonic acid (1) and a dihalogeno benzenes (2) copolymer, although there is no limitation in particular about the molar ratio, when both sum total is set to 1, dihalogeno benzenesulfonic acid (1) is usually 0.01-0.99 -- desirable -- 0.1 to 0.7 -- it is 0.1-0.5 more preferably. It can adjust by adjusting this ratio, the various physical properties, for example, the ion exchange equivalent etc., of polymer, etc.

[0015]A reaction is usually carried out under a solvent. As this solvent, for example Aromatic system solvents, such as benzene, toluene, xylene, and naphthalene, Amide system solvents, such as ether system solvents, such as diisopropyl ether, tetrahydrofuran, 1,4-dioxane, and diphenyl ether, N, N dimethylformamide, and N,N-dimethylacetamide, etc. are mentioned. Two or more sorts of these can also be used. Toluene, tetrahydrofuran, N, N dimethylformamide, and these two or more sorts of mixtures are used preferably especially. 20-200 weight double grade use of the solvent is usually carried out to a monomer.

[0016]The range of polymerization temperature is usually 0-250 **, and it is about 20-100 ** preferably. The range of polymerization time is usually 0.5 to 24 hours.

[0017]Although the poly-phenylene-sulfone acids made into the purpose in this way generate, the extraction from a reaction mixture can apply the usual method. For example, polymer can be deposited by adding a poor solvent and an object can be taken out by filtration etc. It can also refine if needed with the usual refining methods using a flush, and a good solvent and a

poor solvent, such as reprecipitation. The cation exchange of a poly-phenylene-sulfone acid can also use the usual method. Analysis of a degree of polymerization and the structure of polymer can be conducted by the usual means, such as GPC measurement and NMR measurement. Even if the poly-phenylene-sulfone acids of this invention are homopolymers obtained from one sort of monomers, [acids] Even if it is a random copolymer obtained by making two sorts of monomers react simultaneously, it may be an alternating copolymer produced by making two sorts of monomers react gradually, or may be a block copolymer. Although there is no restriction in particular, these degrees of polymerization are usually made into a 10 to 10^4 grade, and molecular weight, and are usually preferred. [of the thing about $10^{6\text{from } 10^3}$]

[0018]Next, the fuel cell using the poly-phenylene-sulfone acids of this invention is explained. Poly-phenylene-sulfone acids are usually used in the state of a film. Although the film production method of this electrolyte membrane does not have restriction in particular, the method (the solution cast method) of producing a film from solution states is used preferably. Under the present circumstances, as a solvent used, the dissolution of poly-phenylene-sulfone acids is possible, If it can remove after that, there will be no restriction in particular, and For example, N, N dimethylformamide, Aprotic polar solvents, such as N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and dimethyl sulfoxide, Dichloromethane, chloroform, 1,2-dichloroethane, chlorobenzene, Alcoholic solvent, such as chlorine-based solvents, such as dichlorobenzene, methanol, ethanol, and propanol, Alkylene glycol monoalkyl ether, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether, and propylene glycol monoethyl ether, water, etc. are mentioned. Two or more sorts of solvents can also be used if needed. As for membranous thickness, although there is no restriction in particular, about 10-200 micrometers is preferred. Thickness is controllable by the solution concentration of poly-phenylene-sulfone acids, or the coating thickness to a substrate top.

[0019]A fuel cell can be manufactured by joining the conductive substance as a catalyst and a current collection object to both sides of the electrolyte membrane which consists of the above poly-phenylene-sulfone acids. As a catalyst, if an oxidation-reduction reaction with hydrogen or oxygen is activable, there is no restriction in particular, and a publicly known thing can be used here, but it is preferred to use the particles of platinum. As for the particles of platinum, it is preferred for it to be supported by the particle state or the fibrous carbon of activated carbon, graphite, etc., and to use. Although a publicly known material can be used also about the conductive substance as a current collection object, the carbon nonwoven fabric or carbon paper of porosity nature is preferred, and can convey material gas to a catalyst efficiently by using these. How to join the carbon which supported platinum particles or platinum particles to the carbon nonwoven fabric or carbon paper of porosity nature, And, [method / of joining it to a

polyelectrolyte film] For example, J. Electrochem. Soc.: The method that the method etc. which are indicated to Electrochemical Science and Technology, 1988, 135 (9), and 2209 are publicly known can be used.

[0020]

[Working example]Although working example is given to below and this invention is explained to it in detail, this invention is not limited at all by these examples.

[0021]Under working example 1 argon atmosphere, in a flask DMF120ml and potassium 1.33g (5.0mmol) 2,5-dichlorobenzenesulfonate, 1.84 g (11.8mmol) of 2,2'-bipyridyl was put in and agitated, then 3.20 g (11.8mmol) of nickel (0) screws (cyclo-octadiene) were added, and it agitated at 60 °C for 3 hours. After radiational cooling, by filling a lot of methanol with reaction liquid, polymer was deposited, it filtered and rough polymer was obtained. After having dissolved the obtained rough polymer in water, filtering the insoluble matter and condensing filtrate, methanol reprecipitation was performed and filtration and the poly-phenylene-sulfone acids 0.56g which carry out reduced pressure drying and are made into the purpose were obtained.

[0022] $^1\text{H-NMR}$ (300 MHz, CDCl_3)

7.3-7.6 Ppm br surface ratio 2.0 (Ar-H)

7.7-8.3 Ppm br surface ratio 1.0 (Ar-H)

GPC (mobile phase: water, PEG conversion)

$M_n = 2300$ and $M_w = 2700$ [0023]Under working example 2 argon atmosphere, in a flask DMF200ml, the 2,5-dichloro benzenesulfonic acid tetrabutylammonium salt 3.6g (7.8mmol), 2.9 g (18.3mmol) of 2,2'-bipyridyl was put in and agitated, then 5.0 g (18.2mmol) of nickel (0) screws (cyclo-octadiene) were added, and it agitated at 60 °C for 3 hours. Reaction liquid was filtered after radiational cooling and rough polymer was obtained. After having dissolved the obtained rough polymer in methanol, filtering the insoluble matter and condensing filtrate, acetone reprecipitation was performed and filtration and the poly-phenylene-sulfone acids 0.81g which carry out reduced pressure drying and are made into the purpose were obtained.

[0024]

$^1\text{H-NMR}$ (300 MHz, CDCl_3) (measurement after acid treatment)

7.2-7.6 Ppm br surface ratio 2.0 (Ar-H)

7.8-8.2 Ppm br surface ratio 1.0 (Ar-H)

GPC (a mobile phase: chloroform, polystyrene conversion)

$M_n = 5500$ and $M_w = 6100$ [0025]Under working example 3 argon atmosphere, in a flask THF200ml, the 2,5-dichloro benzenesulfonic acid tetrabutylammonium salt 1.2g (2.6mmol), 1.8 g (5.2mmol) of 2,5-dibromo-4-isoamyl oxyanisole and 2.9 g (18.3mmol) of 2,2'-bipyridyl were put in and agitated, then 5.0 g (18.2mmol) of nickel (0) screws (cyclo-octadiene) were added,

and it agitated at 60 °C for 3 hours. After radiational cooling, polymer was deposited by filling a lot of methanol with a reaction solution, it filtered, and rough polymer was obtained. After having dissolved obtained rough polymer in chloroform, filtering an insoluble matter and condensing acid cleaning and a chloroform layer for filtrate, methanol reprecipitation was performed and filtration and the poly-phenylene-sulfone acids 0.71g which carry out reduced pressure drying and are made into the purpose were obtained.

[0026]

$^1\text{H-NMR}$ (300 MHz, CDCl_3)

0.9 Ppm br surface ratio 6.0 ($-\text{CH}_3$)

1.6 Ppm br surface ratio 2.0 ($-\text{CH}_2$)

1.7 Ppm br surface ratio 1.0 ($-\text{CH}$)

3.8 Ppm br surface ratio 3.0 ($\text{ArO-CH}_2\text{-C}_4\text{H}_9$)

4.0 Ppm br surface ratio 2.0 (ArO-CH_3)

6.9-7.2 Ppm br surface ratio 2.0 (Ar-H)

GPC (a mobile phase: chloroform, polystyrene conversion)

$M_n = 4700$ and $M_w = 7400$ [0027]

[Effect of the Invention] In this invention, this is polymerized under coexistence of zerovalent transition metal complex using a specific monomer called dihalogeno benzenesulfonic acid. Therefore, moreover, poly-phenylene-sulfone acids can be manufactured easily at once. The electrolyte membrane which consists of obtained poly-phenylene-sulfone acids shows performance high as diaphragms, such as a polymer electrolyte fuel cell.

[Translation done.]